© 1999 The Chemical Society of Japan

Bull. Chem. Soc. Jpn., 72, 357—362 (1999)

Rate-Determining Step of Deswelling for Conventional and Macroporous Poly(*N*-isopropylacrylamide) Gels

Norihiro Kato and Fujio Takahashi*

Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University,
2753 Ishii-machi, Utsunomiya 321-8585

(Received August 11, 1998)

The kinetic parameters of deswelling for conventional and macroporous poly(*N*-isopropylacrylamide) gels were determined in order to point out the rate-determining step on the deswelling process in a NaCl or KCl solution. The apparent activation energy for the deswelling of the conventional gel in water (130 kJ mol^{-1}) was larger than that of the macroporous gel in water (25 kJ mol^{-1}). The split process of the skin layer, which was formed on the surface of the gel by heating from outside of gel, was considered concerning the rate-determining step in the case of the conventional gel. The activation entropy changes at 313 K (ΔS_{313}'s) of the macroporous gel were determined to be -65 J K^{-1} mol^{-1} in 0.1 M NaCl (1 M = 1 mol dm^{-3}), of which the cation exhibits a structure-forming property, and 180 J K^{-1} mol^{-1} in 0.1 M KCl, of which the cation exhibits a structure-breaking property. The sign of ΔS_{313} for the macroporous gel was negative at higher than 0.3 M NaCl or KCl. In order to point out the rate-determining step, the process of the salting-out effect, that of bond formation between the polymer chains, and that of forming water clusters in the presence of the cation inside of the gel are discussed.

There have been many papers concerning the deswelling mechanism of poly(*N*- isopropylacryamide) gel, poly(NIPAAm) gel, in connection with the lower critical solution temperature (LCST) and the hydrophobic interaction.[1—5] The deswelling kinetics of poly(NIPAAm) gel was investigated by comparing the conventional and macroporous structures of the polymer network.[6,7] By freeze-dry and hydration treatments, the poly(NIPAAm) gel changed to the macroporous structure and the deswelling rate increased to approximately 10^2-times faster than the gel without a freeze-dry treatment. It was speculated in our previous paper that the diffusion area increased and a hydrophobic "skin" layer was not formed in the macroporous gel.[6]

Park and Hoffman described in their paper that a dense hydrophobic barrier was formed at the surface of the gel due to heating the gel from the surrounding of the gel, and that the diffusion rate of water through the skin layer was associated with the rate-determining step of the deswelling for the conventional poly(NIPAAm) gel.[8] On the other hand, it was suggested from our deswelling profile that the conventional gel deswelled in a two-stage process consisting of a slow release of water (due to the skin) at first, and then a rapid release of water. However, no evidence could be obtained for deciding the rate-determining step.

The macroporous gel might deswell under a different rate-determining step compared with that of the conventional gel. The apparent activation energy (E_a) and the activation entropy change (ΔS_{313}) of the deswelling of the macroporous gel have already been reported.[7] However, the relationship between the rate-determining step and the kinetic parameters (E_a and ΔS_{313}) was not clear.

In this paper, we present the results concerning the kinetic parameters for the deswelling of the conventional gel in NaCl and KCl solutions in order to make a comparison with the macroporous gel. Both alkalimetal chlorides were used as a probe in order to investigate the mechanism of gel deswelling. It is discussed concerning the difference in the rate-determining step for deswelling between the conventional gel and the macroporous gel.

Experimental

Materials. *N*-Isopropylacrylamide was purchased from Tokyo Kasei Kogyo. All other chemicals were of guaranteed grade or the best commercially available.

Preparation of Poly(NIPAAm) Gel. The conventional poly(NIPAAm) gel, crosslinked by *N,N'*-methylenediacrylamide, was prepared in a 0—0.6 M (1 M = 1 mol dm^{-3}) NaCl or KCl solution in the same way as that described in previous papers.[6,7] Polymerization was carried out in a silicone tube (ϕ = 2 or 3 mm) in order to form a rod of the gel. All of the gel rods were equilibrated in water or a NaCl or KCl solution at 22 °C before conducting experiments.

Measurement of the Deswelling Rate. The initial deswelling rate of the conventional gel was determined in the same manner as for the macroporous gel.[7] A gel rod (L_o = 50—60 mm) equilibrated in various concentration of NaCl or KCl solution at 22 °C was transferred to the same solution at the required temperature (T = 30—55 °C). The change in the gel rod length (L) was measured on a picture recorded by video-tape. The initial deswelling rate, $-\mathrm{d}(L/L_o)^3/\mathrm{d}t$, was determined from the slope of the line obtained by plots of $(L/L_o)^3$ against time, where L_o is the initial length of the gel rod at 22 °C. The apparent activation energy (E_a) and the activation entropy change at 313 K (ΔS_{313}) were calculated according to the Arrhenius equation.

Results

Diameter Dependence of the Deswelling Kinetics. A measurement of the deswelling for the conventional gel was carried out using a gel with ϕ = 1—4 mm in a KCl solution. In the case of a gel with ϕ = 1 mm, a similar result was obtained compared with a gel with ϕ = 2 mm. In the case of a gel with ϕ = 4 mm, the gel rod was found to split out during the deswelling process. Therefore, the deswelling profile could not be obtained.

The deswelling profiles for the conventional gels with ϕ = 2 mm in various concentrations of KCl solution are shown in Fig. 1. Different time lags (plateaus for the deswelling profiles) were observed between the first- and second-stage deswelling. The length of time lag or plateau increased with increasing the KCl concentration. The skin layer (small bubbles at the surface of the gel) was observed a few minutes after heating in a 0.6 M KCl solution, as shown in Fig. 2, and a deswelling occurred after 15 min in this case. The skin layer of the gel split out after the time lag and slowly disappeared with deswelling. The time lag was likewise observed in the case of gels with ϕ = 2 mm in the NaCl solution (Fig. 3). Okano et al. reported on a similar phenomenon based on photographs of poly(NIPAAm-*co*-butyl methacrylate) gels.[9]

On the other hand, neither the skin layer nor the time lag was observed in the deswelling profiles of the gels (ϕ = 3 mm) in a 0.3 M KCl solution at different temperatures (Fig. 4A). As shown in Fig. 4B, two-stage deswelling was observed for the gel (ϕ = 2 mm) in a 0.3 M KCl solution. The deswelling rates, $-\mathrm{d}(L/L_{\mathrm{o}})^3/\mathrm{d}t$'s, were given as the slope of the solid line in Fig. 4. The deswelling rates were obtained from the first stage, except for the gels (ϕ = 2 mm) in a 0.3 M KCl or NaCl solution. In the case of the exceptions, the

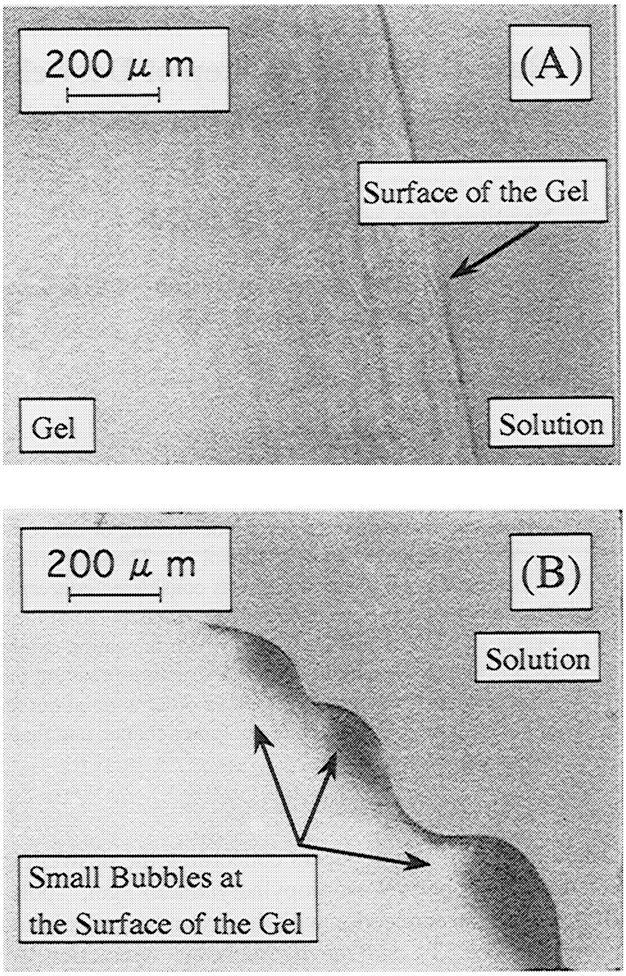

Fig. 2. Photomicrographs of the conventional gel (ϕ = 2 mm) before (A: 0 min) and after (B: 5 min) heating. The gel rod equilibrated at 22 °C was heated to 40 °C in 0.6 M KCl solution.

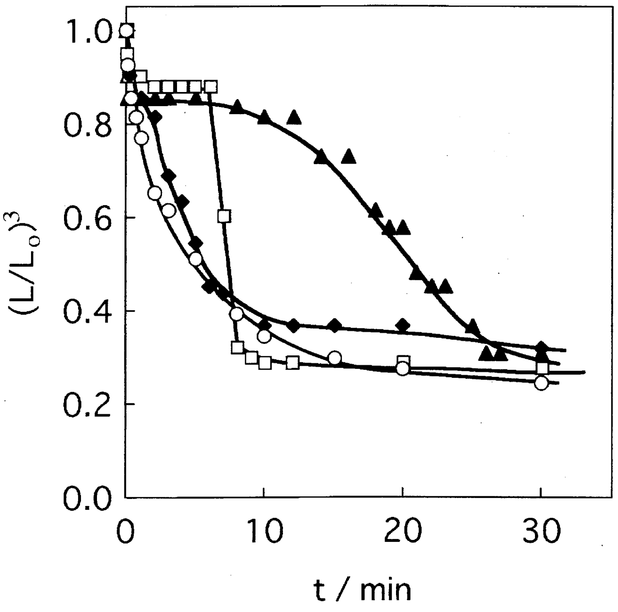

Fig. 1. Deswelling profiles of the conventional poly(NIPAAm) gel (ϕ = 2 mm) in a KCl solution: ○ 0.1 M, ◆ 0.2 M, □ 0.4 M, ▲ 0.6 M. The gel rod equilibrated at 22 °C was transferred to the same solution at 40 °C.

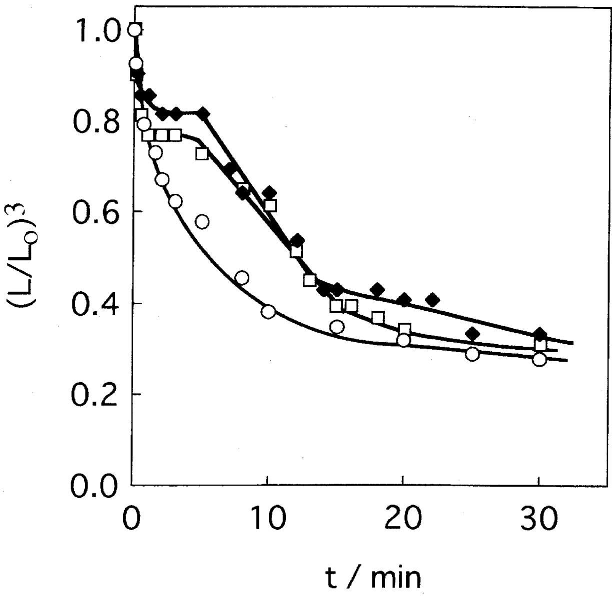

Fig. 3. Deswelling profiles of the conventional poly(NIPAAm) gel (ϕ = 2 mm) in NaCl solution: ○ 0.1 M, □ 0.2 M, ◆ 0.3 M. The gel rod equilibrated at 22 °C was transferred to the same solution at 40 °C.

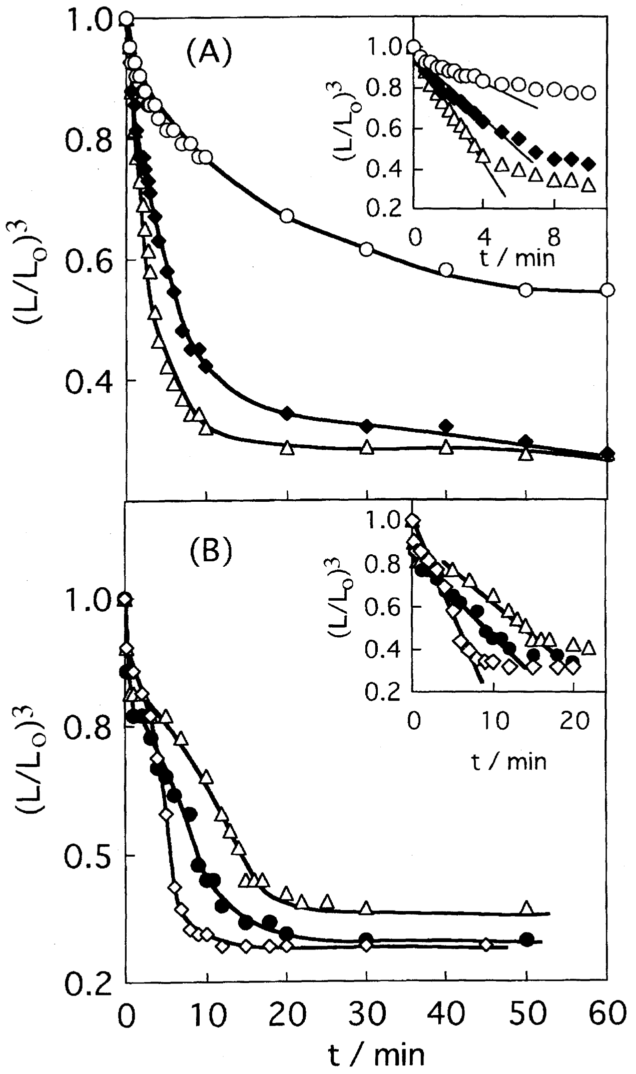

Fig. 4. Deswelling profiles for the conventional poly(NIPAAm) gel of $\phi = 3$ (A) and $\phi = 2$ mm (B) in 0.3 M KCl solution. (A): The gel rod equilibrated at 22 °C was transferred to the same solution at 30 °C (○), 36 °C (◆), and 40 °C (△). (B): The gel rod equilibrated at 22 °C was transferred to the same solution at 40 °C (◇), 50 °C (●), and 55 °C (△).

second stage after a short time lag was used for determining the deswelling rates.

E_a and ΔS_{313} for the Conventional Gel. Arrhenius plots of various concentrations of KCl and NaCl solutions are shown in Figs. 5 and 6. The E_a's and ΔS_{313}'s were obtained according to the Arrhenius equation using the lines in Figs. 5 and 6. The values of the E_a's for the conventional gel are plotted against the concentration of KCl and NaCl in Fig. 7. For a comparison with the macroporous gel, the data of our previous paper are inserted in Fig. 7.[7] It was found that E_a for the conventional gel ($\phi = 3$ mm) decreased with increasing the concentration of KCl. Similarly, the values of ΔS_{313}'s are given in Fig. 8.

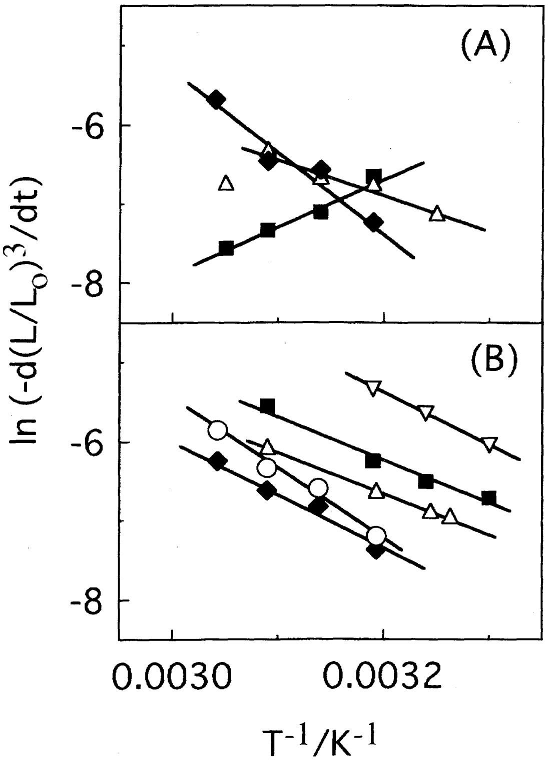

Fig. 5. The Arrhenius plots on the conventional gels of $\phi = 2$ (A) and $\phi = 3$ mm (B) in KCl solution: ○ water, ◆ 0.1 M, △ 0.2 M, ■ 0.3 M, ▽ 0.6 M.

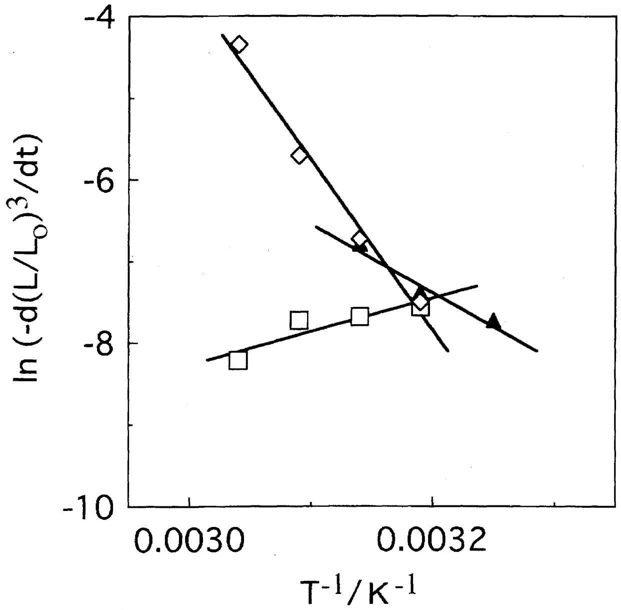

Fig. 6. The Arrhenius plots on the conventional gels of $\phi = 2$ mm in NaCl solution: ◇ 0.1 M, ▲ 0.2 M, □ 0.3 M.

Discussion

Time Lag of the Deswelling Process. A skin layer was formed on the surface of gel by heating the conventional gel.[6,8] The split of the skin layer was driven under the pressure of deswelling. This fact was explained by assuming that the pressure of deswelling depended upon the strength

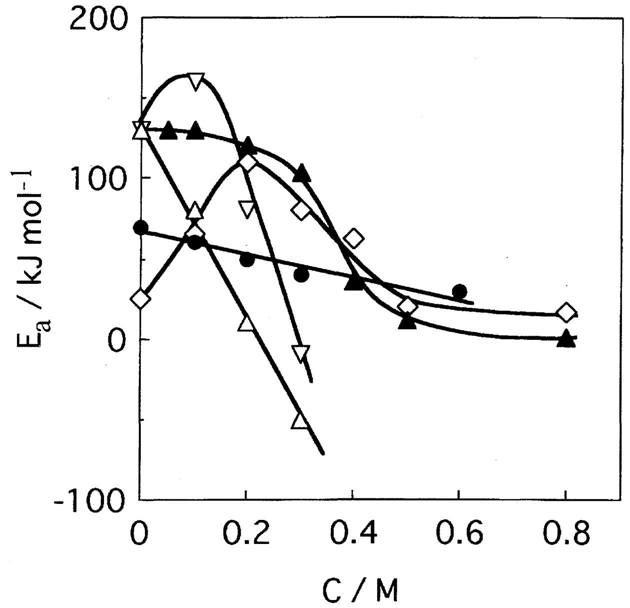

Fig. 7. The apparent activation energy (E_a) of the deswelling for the conventional and the microporous gel in salt solution. Conventional gel: ● KCl (ϕ = 3 mm), △ KCl (ϕ = 2 mm), ▽ NaCl (ϕ = 2 mm). Macroporous gel: ▲ KCl (ϕ = 2 mm), ◇ NaCl (ϕ = 2 mm).

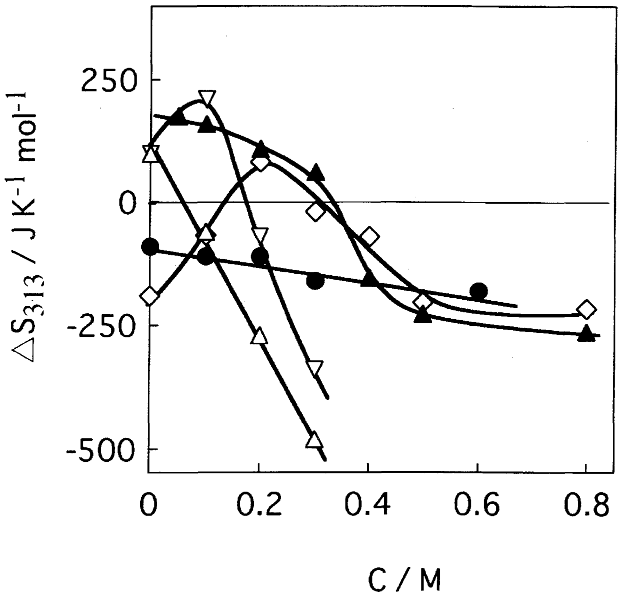

Fig. 8. The activation entropy change (ΔS_{313}) of the deswelling for the conventional and the macroporous gel in salt solution. Conventional gel: ● KCl (ϕ = 3 mm), △ KCl (ϕ = 2 mm), ▽ NaCl (ϕ = 2 mm). Macroporous gel: ▲ KCl (ϕ = 2 mm), ◇ NaCl (ϕ = 2 mm).

for squeezing water out of the gel, and that the length of the time lag became longer with decreasing the pressure before deswelling. Since gel rods with ϕ = 3 mm have a larger ratio of volume-to-surface area than those of ϕ = 2 mm, as shown in Table 1, the former can pass a 1.5-times larger amount of water through the surface area of the gel than the latter. This corresponded to the pressure of deswelling. It was considered that the pressure of deswelling might be strong enough for gel rods with ϕ = 3 mm, but not for a gel with ϕ = 2 mm. Therefore, a weak pressure inside ϕ = 2 mm gel rods produced a time lag before the second-stage deswelling for splitting the skin layer of the gel.

Table 1. The Volume and Surface Area of the Column (L = 50 mm)

ϕ/mm	V/mm^3	S/mm^2	V/S/mm
2	157	320	0.49
3	353	485	0.73

Effect of the KCl Concentration on the E_a's and ΔS_{313}'s for the Conventional Gel with ϕ = 2 and 3 mm. In both cases with ϕ = 2 and 3 mm, E_a decreased linearly with

Table 2. The E_a's and the ΔS_{313}'s for Conventional and Macroporous Poly(NIPAAm) Gels and the Rate-Determining Step

	ϕ mm	Salt	$-d(L/L_o)^3/dt$ 1) s^{-1}	E_a kJ mol^{-1} 0	E_a kJ mol^{-1} 0.1 M 2)	ΔS_{313} J K^{-1} mol^{-1} 0	ΔS_{313} J K^{-1} mol^{-1} 0.1 M 2)	Effect on water structure	Rate-determining step for deswelling
Conventional gel	2	Water 3)	5.9×10^{-4}	130	—	100	—		Split of skin layer.
		NaCl	6.1×10^{-4}	—	160	—	210	Forming	Split of skin layer. Additional effect of structure-forming cation
		Kcl	7.2×10^{-4}	—	80	—	−60	Breaking	Split of skin layer.
	3	Water	7.5×10^{-4}	70	—	−90	—		Split of skin layer. Stronger pressure of water squeezing out.
		Kcl	6.3×10^{-4}	—	60	—	−110	Breaking	Split of skin layer.
Macroporous gel 3)	2	Water	0.17	25	—	−190	—		Bond formation between polymer chains.
		NaCl	0.11	—	65	—	−65	Forming	Bond formation between polymer chains.
		Kcl	0.098	—	130	—	180	Breaking	Dissociation of hydrated water to polymer segments.

1) In 0.1 M salt solution at 40 °C. 2) Higher than 0.3 M, salting-out effect predominant. 3) Cited from our previous papers.6,7)

increasing the concentration of KCl (Fig. 7). The deswelling rates were influenced by salting-out in both the conventional gel and the macroporous gel. This effect gave rise to E_a's decrease.[7)] The higher was the KCl concentration, the greater was the salting-out effect; in turn, the smaller were the E_a's. The E_a's in the cases of gel with ϕ = 2 and 3 mm were different at zero concentration of KCl. E_a of the gel with ϕ = 2 mm (130 kJ mol^{-1}) was larger than that with ϕ = 3 mm (70 kJ mol^{-1}). It seemed that an additional energy for splitting the skin layer was necessary for a gel with ϕ = 2 mm.

The results of the ΔS_{313}'s (Fig. 8) showed a similar tendency compared to as those with E_a's. The ΔS_{313} of a gel with ϕ = 2 mm was positive, while that with ϕ = 3 mm was negative at zero concentration of KCl. This fact indicates that a stronger pressure inside the gel might accelerate the squeezing of water out to form hydrophobic bonding between the polymer chains, of which the bonding made ΔS_{313} negative.

Difference between NaCl and KCl on the Conventional Gel. There is a maximum of E_a in case of NaCl in Fig. 7. The potassium ion is known to exhibit a water structure-breaking property, while Na^+ acts as a structure-forming ion. Therefore, it was considered that a water structure-forming property influenced predominantly inside the gel below 0.2 M NaCl. The ΔS_{313} of 0.1 M NaCl was positive, as shown in Fig. 8. The rate-determining step of deswelling might be different between structure-forming and structure-breaking circumstances inside the gel.

Comparison between the Conventional Gel and the Macroporous Gel. The results concerning the E_a's and ΔS_{313}'s of the conventional gel were compared with those of the macroporous gel reported in a previous paper.[7)] The results are summarized in Table 2. The deswelling rate of the macroporous gel was about 10^2-times faster than that of the conventional gel. It was speculated that the pore size on the surface of the macroporous gel was larger than that on the conventional gel. Consequently, water release became easier with a larger pore size of the gel.

In the case of the macroporous gel discussed in the previous paper, the maxima of the E_a's and ΔS_{313}'s at around 0.2 M Cl^- could be explained by an electrostatic repulsion between the Cl^- ions, which might disturb the intermolecular interaction between the polymer segments.[7)] The results of the conventional gel in Figs. 7 and 8 could be explained in the same way.

Rate-Determining Step of Deswelling. The E_a's obtained from the second-stage deswelling are negative in Fig. 4B. The process of the first stage was considered to cause the rate-determining step. It seemed that the deswelling process consisted of the first stage followed the second stage after splitting the skin layer of the gel.

The sign of ΔS_{313} was considered to be an important factor concerning the rate-determining step. In the case of the conventional gel deswelling in water, it was estimated that the rate-determining step involved the split process of the skin layer, because the sign of ΔS_{313} was positive; further, E_a was larger than that in the case of the macroporous gel deswelling in water. On the other hand, the rate-determining step in the deswelling of the macroporous gel should be different, because the sign of ΔS_{313} was different.

Some ΔS_{313} salt-concentration curves were placed in both positive and negative regions. The salting-out effect might be predominantly for the deswelling process at higher than 0.3 M NaCl or KCl. Since ΔS_{313} was negative at higher than 0.3 M NaCl or KCl, the rate-determining step was considered to involve the bond-formation process between the polymer chains.

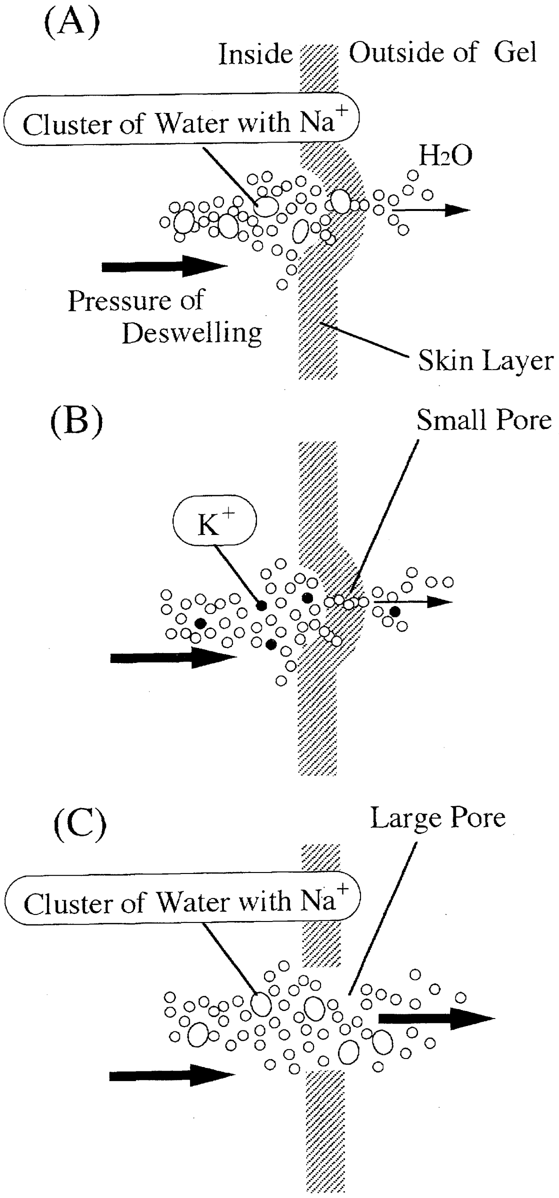

Fig. 9. Schematic illustrations of the water release. Conventional gels in NaCl (A) or KCl solution (B). The process for split of the skin layer makes the rate-determining step. The structure-forming property of Na^+ ion pushed up the E_a as compared with K^+ ion breaking water structure. (C) Macroporous gel in NaCl solution. It is easy for the cluster to pass through the large pore.

In the region of lower than 0.3 M NaCl or KCl, the water structure inside the gel was considered to involve the rate-determining step. A cluster of water might be formed inside a gel containing 0.1 M NaCl, of which the Na^+ ion exhibits a structure-forming property. On the contrary, the K^+ ion, acts as a structure-breaking cation, which is known to be weak in order to attract water molecules surrounding the polymer chains, compared with Na^+. E_a could alter the influence of the thickness or density of the skin layer, the size of the cluster, and the pressure for squeezing water out. Since the plateau was not observed for the conventional gels in 0.1 M NaCl and KCl solutions (Figs. 1 and 3), the skin layer under this condition was not so tough that the cluster could pass through the skin layer. The difference for the toughness of the skin layers between being in a NaCl or KCl solution was not quantified from the kinetic measurements, while the cluster in NaCl solution was larger than that in the KCl solution.

On the other hand, the effect of the toughness of the skin layer could be excluded for the macroporous gels. According to Table 2, the opposite sign was obtained for ΔS_{313} of 0.1 M NaCl and 0.1 M KCl. The former was negative and the latter was positive. Judging from the sign of ΔS_{313}, the rate-determining step upon deswelling of the macroporous gel might be the bond-formation process between the polymer chains in the case of Na^+ and the dissociation process of hydrated water to polymer segments in the case of K^+.

In conclusion, a schematic illustration of the rate-determining step is shown in Fig. 9, which is a modified version of the figure shown in a previous paper.[6)]

In the previous paper, the E_a's and the ΔS_{313}'s of deswelling in six alkalimetal halides were reported. These alkalimetal halides were classified into two groups (Group A and B), as follows. The ΔS_{313}'s for deswelling of the macroporous gel was estimated to be around 100 $\mathrm{J\,K^{-1}\,mol^{-1}}$ at lower than 0.1 M salt solution of group A (KCl, NaBr, NaI) and -190 $\mathrm{J\,K^{-1}\,mol^{-1}}$ in those of group B (NaF, NaCl, LiCl). The ΔS_{313}'s of group A were in accord with those of the conventional gel in water. The structure-breaking ion (K^+, Br^-, I^-) of group A was thought to control the rate-determining step for deswelling of the macroporous gel. It was concluded that classifying alkalimetal halide could be applied in the present data without any contradiction.

References

1) M. Shibayama, S. Mizutani, and S. Nomura, *Macromolecules*, **29**, 2019 (1996).

2) K. Otake, H. Inomata, M. Konno, and S. Saito, *Macromolecules*, **23**, 283 (1990).

3) S. Hirotsu, *J. Phys. Soc. Jpn.*, **56**, 233 (1987).

4) H. Inomata, S. Goto, K. Otake, and S. Saito, *Langmuir*, **8**, 687 (1992).

5) T. G. Park and A. S. Hoffman, *Macromolecules*, **26**, 5045 (1993).

6) N. Kato and F. Takahashi, *Bull. Chem. Soc. Jpn.*, **70**, 1289 (1997).

7) N. Kato and F. Takahashi, *Bull. Chem. Soc. Jpn.*, **71**, 1299 (1998).

8) T. G. Park and A. S. Hoffman, *J. Appl. Polym. Sci.*, **52**, 85 (1994).

9) T. Okano, Y. H. Bae, H. Jacobs, and S. W. Kim, *J. Controlled Release*, **11**, 255 (1990).